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Dia-Magnetic to Ferro-Magnetic Behavioral Change of Fe-Catalysts Based Nitrogenated Carbon Nanotubes (NCNTs) by the Process of Chlorination/Oxidation

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In this work, we have synthesized multiwall nitrogenated carbon nanotubes (MW-NCNTs) with Fe-catalysts by the microwave plasma-enhanced chemical vapor deposition process@950 °C and subsequently functionalized with chlorine and oxygen. The dia-magnetic behavioral M-H loop of non-functionalized MW-NCNTs were turn into ferromagnetic behaviors by the process of chlorination and oxidation respectively; which were characterized by means of superconducting quantum interference device magnetometer within the temperature range 5–300 K. A prominent cusp like behavior is also observed at around ≈45 K in M_{FC} and M_{ZFC} measurements confirming the ferromagnetic behaviors of these MW-NCNTs after chlorination and oxidation.

Keywords: Dia and Ferro Magnetism, N-CNTs, Chlorination and Oxidation.

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1. INTRODUCTION

Carbon nanotubes (CNTs) have been of great interest because of their unique structural, electrical and mechanical properties. Due to these extraordinary properties it provides potential applications on the nanometer scale that include nano-devices, quantum wires, ultrahigh-strength engineering fibers, sensors and catalyst supports.[1–3] To optimize the uses of nanotubes in many of these applications, it is necessary to decorate the surface of CNTs. In recent years, the intrinsically nanosized morphology has also initiated research on applications in the field of magnetism. In particular, encapsulation of iron nano-particles and/or nanowires in CNTs shows highly anisotropic behavior that were discussed for a wide range of potential applications.[4,5] Various studies shown that the carbon encapsulated iron is efficiently protected by the surrounding shells and their magnetic properties are retained.[6] The fact that the magnetic filling material is protected against the environment so that increased wear resistance is realized while oxidation is inhibited. Magnetically filled CNTs are also widely used in the biomedical applications, where the carbon shielding prevents degradation of the filling materials and their potential toxicity and adverse effects are suppressed. Particular, magnetic imaging and targeted hyperthermia therapy with magnetically filled CNTs can be envisioned[7,8] and even CNTs can be utilized as drug delivery agents.[9,10] To study in detail about the magnetic properties of a filling material or to utilize CNTs as a highly pure nonmagnetic agent for biological environments, nonmagnetic CNTs have to be available. The growing of CNTs is however a catalyzed-determined process. The most used catalyst materials are the Fe, Co, and/or Ni. In general, all these metals show over a wide temperature range ferromagnetic properties. Hence, alternative techniques have to be developed in order to either remove completely the catalyst material from the nanotubes or to apply nonmagnetic catalysts. Various purification methods have been employed to remove magnetic impurities, such as chemical treatment, microwave heating, mechanical filtration, and heat treatment in a vacuum or oxidative environment.[11–14] However, a graphitic coating commonly found around ferromagnetic catalyst particles shields the particles from acid dissolution. Attempts to remove this graphitic coating often result in damage or destruction of SWNTs.[14] Although some groups applied magnetic filtration, the efficiency was low such that ferromagnetism still dominated the magnetic moment of the sample for fields of order a few Tesla.[15–18] To circumvent this problem, other researchers synthesized nanotubes using non-ferromagnetic catalysts such as Rh/Pd or Rh/Pt.[19] Lipert et al.[20] shows two different ways to obtained CNTs having diamagnetic behaviors (nonmagnetic). Those two processes are post synthesis evaporation of catalyst particles

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at extremely high temperatures and synthesis of CNTs using diamagnetic catalyst materials like Re. However, the purification methods are insufficient to achieve the levels of purity necessary for different applications and for the study of standard non enriched nanotube materials. The high cost and low yield of CNTs materials provided by these methods make them ill-suited for mass production. In this present work, we prepared the MW-NCNTs that behaves diamagnetic behavior and hence functionalized with chlorine and oxygen which also shows strong diamagnetic behaviors that could be very use full for different bio-application that were mentioned above. In this process, we were initially synthesized vertically oriented nitrogenated multiwall carbon nanotubes (MW-NCNTs) by the microwave plasma-enhanced chemical vapor deposition (PECVD) process on silicon substrates pre-coated with an *e*-beam evaporated thin Fe catalytic layer.[21] Then, obtained N-CNTs were chlorinated in an inductively plasma coupled reactor in flowing Cl-gas.[22] Whereas oxidation were performed under air-atmospheric plasma conditions using a dielectric barrier discharge system.[23] We observed that at room temperature all these MW-CNTs shows diamagnetic behaviors.

2. EXPERIMENTAL DETAILS

The dia-/ferro- magnetic behavioral change M-H loops were measured at 5 K and 300 K respectively; whereas the zero-field cooled (ZFC) and field cooled (FC) measurements were carried out from room temperature down (300 K) to 5 K using quantum design superconducting quantum interference device (SQUID) magnetometer. The details of functionalized (Cl/O)/non-functionalized MW-NCNTs could be found elsewhere.[21–23]

3. RESULTS AND DISCUSSION

Figures 1(a–c) show the typical scanning electron miscroscopy (SEM) images of N-CNT, N-CNT:Cl, and N-CNT:O, respectively.

It is clearly observed from the cross sectional SEM images that the vertical alignment of N-CNT is changed on chlorine-plasma treatment, but strong vertical alignment is formed when the treatment was performed with oxygen-plasma. In general, the mechanism of the highly vertically aligned growth is mainly attributed to the high density of CNT being grown from the densely packed catalytic nanoparticles. As the nanotubes lengthen, they interact with nearby nanotubes, presumably by van der Waals forces, to form a large bundle with some rigidity, which enables them to keep growing along the same direction.[12] On the basis of this growth mechanism, the alignment is changed on chlorine/oxygen-plasma treatments. Simultaneously, the density as well as the lengths of the tubes is decreased on chlorination, but on oxidation it increased;

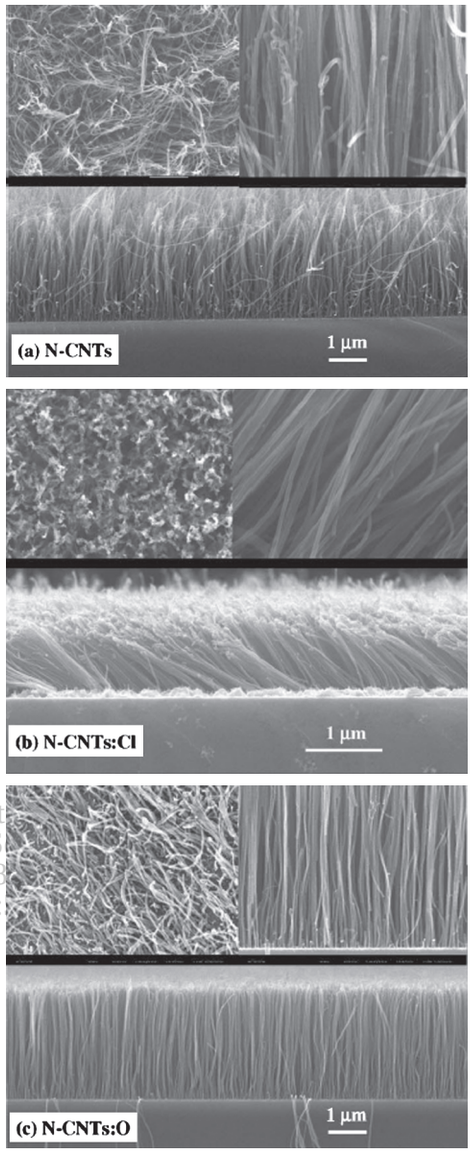

Fig. 1. Scanning electron microscopy of (a) MW-CNTs (b) Chlorine functionalized MW-CNTs and (c) Oxygen functionalized MW-CNTs.

those can be observed from the overview and cross-section SEM images shown in Figure 1. The increase (decrease) in length and density of the nanotubes can be explained with respect to their growth mechanism. The diffusion and precipitation of the reactive carbon species are faster (slower) in oxidation (chlorination), resulting in faster (slower) growth rate and increase (decrease) in nanotubes length as well as nanotubes density. During the process of oxidation (chlorination), probably larger (smaller) numbers of active carbon species are in nucleation site that enhance (reduce) the nanotubes density. However, it seems that the diameters of the tubes are slightly increased (∼29 nm) and decreased (∼21 nm) on chlorine and oxygen treatments,

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respectively, with respect to non-treated N-CNT (∼26 nm) due to a change in CNT density.

The magnetization M-H hysteresis loop of MW-NCNTs obtained at 300 K and 5 K is shown in Figure 2(a). The spectral features behavior unambiguously implies a diamagnetic response, although the CNTs have contribution of magnetic Fe-particles. We emphasize that the spectra at $T = 5$ K strongly confirms the diamagnetic behavior of this N-CNTs. Lipert et al.[24] observed the similar diamagnetic behavior of Fe-based MWCNTs, after post annealing process at 2500 °C temperature. They have claimed that the ferromagnetic behavior changed into diamagnetic due to complete evaporation of Fe-catalyst particles from the CNTs at this higher annealing temperature. But, we do follow any post annealing process and shows diamagnetic behavior as synthesized CNTs that shown in Figure 2(a). Furthermore, the chlorine and oxygen functionalized MW-NCNTs shows the ferromagnetic behavioral M-H hysteresis loop unlike non-functionalized MW-NCNTs as shown in Figure 2(b and c). Bianco et al.[25] also observed the ferromagnetic behavioral M-H loop for the core interface of oxygen passivated Fe-nano-particles. In our case it may occur due to both of chlorine as well as oxygen passivation with the N-CNTs on oxidation as well as chlorination.

The thermal evolution of the magnetization measurements temperature (T) dependence magnetization (M) were further characterized for all CNTs (functionalized/non-functionalized) by the zero-field-cooling (M_{ZFC}) and field-cooling (M_{FC}) procedures in an applied magnetic field of 50 Oe, 200 Oe and 1000 Oe respectively in between 5 K and 300 K. Figure 3(a) shows the M-T curve of N-CNTs; whereas N-CNT:Cl and N-CNTs:O shown in Figure 3(b and c) respectively. It shows the M_{ZFC} curve gradually deviates from the M_{FC} curve with decrease of temperature at about 280 K, when magnetic field is applied 50 Oe for the N-CNTs and is further decrease to 255 K at the applied magnetic field 1000 Oe. Upon further cooling, the M_{ZFC} plot exhibits a cusp centered at about 45 K, and the M_{FC} data sequentially increases when magnetic applied field was changed from 50 to 1000 Oe as shown in Figure 3(a). This variable temperature magnetic data clearly indicate that the Fe/N-CNTs exhibit weak ferromagnetic behavior at below room temperature, which is attributed to the uncompensated surface spin states or ferromagnetic Fe clusters. As a result, it is believed that the weak ferromagnetic performance of the Fe/N-CNTs comes from the ferromagnetic Fe clusters and the uncompensated surface spin states.

This low temperature ferromagnetic phase magnetization is correlated to the fact that at lowest temperature and after M_{ZFC} process, the moments of magnetic particle Fe are not fully aligned with the applied field. Furthermore, no cusp is observed in the M_{ZFC} plot in N-CNT:Cl line N-CNTs indicating that after functionalization with chlorine (N-CNT:Cl), it becomes more diamagnetic in nature.

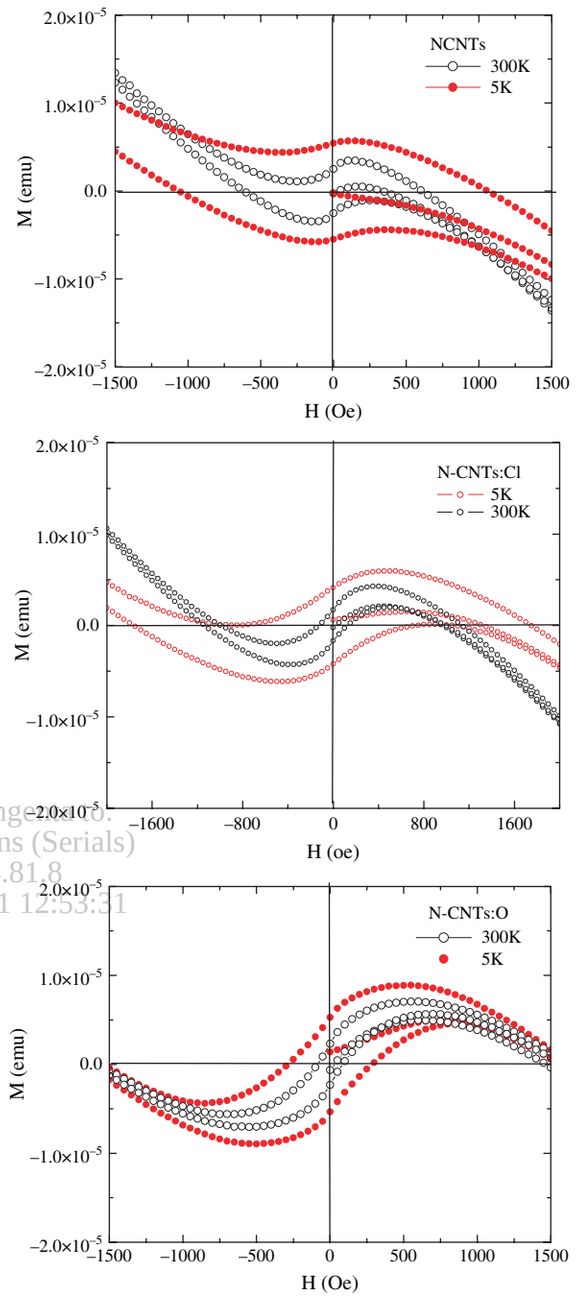

Fig. 2. M-H hysteresis loop of (a) MW-CNTs (b) Chlorine functionalized MW-CNTs and (c) Oxygen functionalized MW-CNTs.

In case of N-CNT:O, it is found that the M_{ZFC} curve gradually deviated from the M_{FC} curves with decrease of temperature at about 300 K as shown in Figure 3(c), when measured at an applied magnetic field of 1000 Oe. A similar behavior has been observed by Zhang et al.[27] for CoO/CNTs core–shell nanostructures, when they have measured at an applied magnetic field 100 Oe between 2 K and 300 K. In our present case, it is also further observed upon further cooling that the M_{ZFC} plot exhibits a cusp centered at about ≈45 K and the M_{FC} data sequentially

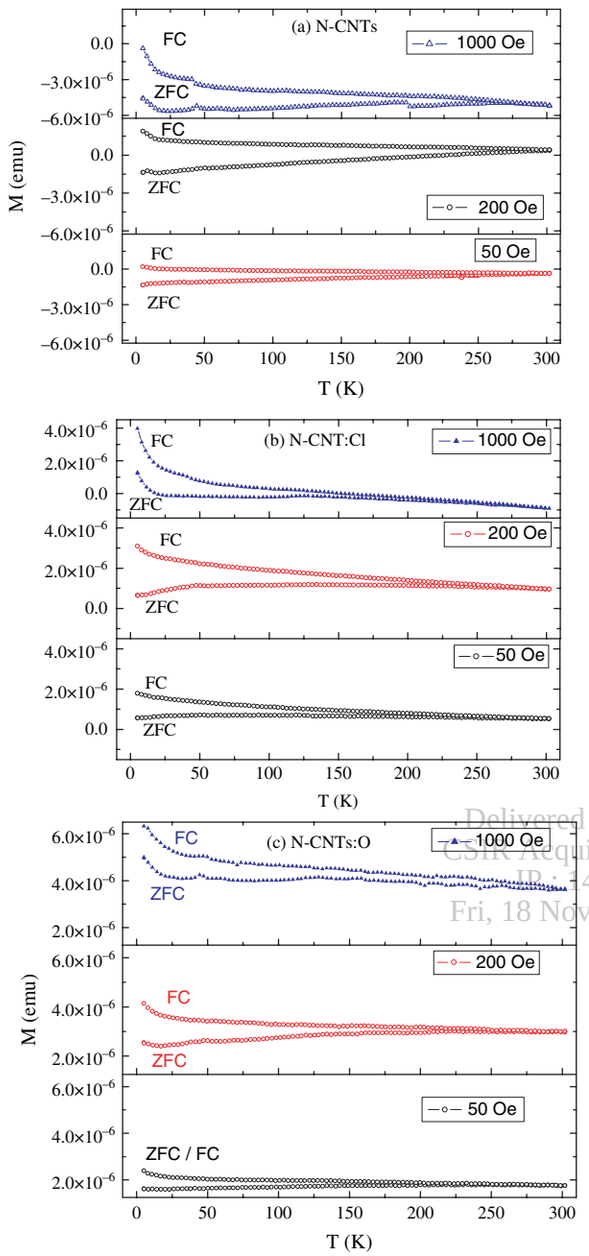

Fig. 3. M_{FC} and M_{ZFC}, M-T spectra of (a) MW-CNTs (b) Chlorine functionalized MW-CNTs and (c) Oxygen functionalized MW-CNTs.

increases indicates higher ferromagnetic behavior at this temperature compared to N-CNT and N-CNT:Cl. It is believe that this ferromagnetic behavior comes from the ferromagnetic Fe-clusters and uncompensated surface spin states, although M-H curve shown in Figure 1 is completely diamagnetic in nature.

4. CONCLUSION

Room temperature diamagnetic behaviors have been studied for the N-CNTs and functionalized N-CNTs with oxygen and chlorine. The interaction between Fe-nanoparticles and the CNTs plays a critical role for the diamagnetic behavior of the Fe-catalyst based N-CNTs at room temperature. A very week ferromagnetic nature shows at lower temperature and is due to ferromagnetic Fe-clusters and the uncompensated surface spin states. It is believe that these magnetic N-CNTs (:Cl/O) may show promising applications in biomedicine and other bio-applications.

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